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Crystal field study of Gd^{3+}-doped La$_x$RE$_{1-x}$F$_3$ (RE = Ce, Pr, Nd) single crystals

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ABSTRACT

The mixed La$_x$RE$_{1-x}$F$_3$ (RE = Ce, Pr, Nd) single crystals doped with Gd^{3+} (0.1 mol%) were grown by a modified Bridgmann-Stockbarger method. The crystal field was investigated using electron paramagnetic resonance technique. The angular dependencies of Gd^{3+} ($^8S_{7/2}$, f^7) line positions with magnetic field oriented in (001) plane were measured in the temperature range 4.2 – 295 K. The surroundings of Gd^{3+} ions were investigated analyzing spin-hamiltonian parameters in the light of the superposition model. The small distortion of the D_{3d}^4 trigonal symmetry has been observed in LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$ and La$_{0.9}$Nd$_{0.1}$F$_3$ below 150 K. The local structure deformation of the site symmetry of Gd^{3+} ions induced by temperature starts at about 150 K becoming larger at 4.2 K. In PrF$_3$ the distortion was not observed in the temperature range 4.2 – 295 K. The results were compared with those of Gd^{3+}-doped LiYF$_4$ crystals.

Keywords: rare-earth trifluorides, electron paramagnetic resonance (EPR), spin-hamiltonian parameters, zero-field splitting, distortions, magnetic ordering.

1. INTRODUCTION

The La$_x$RE$_{1-x}$F$_3$ (RE = Ce, Pr, Nd) single crystals are utilized as laser materials and radiation hard scintillators for calorimetry at future colliders.[1-4] The mixed La$_x$Ce$_{1-x}$F$_3$ single crystals can also be used as the filters for the vacuum ultraviolet.[5] The single crystals doped with Gd^{3+} (0.1 mol%) were grown by a modified Bridgmann-Stockbarger method described elsewhere.[6,7] The $^8S_{7/2}$ ground term of the Gd^{3+} ion in these single crystals is split by the crystalline electric field into four Kramers doublets. It is important to know how the crystal field splits this term at various temperatures. The small distortion from the D_{3d}^4 trigonal space group, caused by the strong influence of the crystalline field, was observed in La$_x$Ce$_{1-x}$F$_3$ and La$_x$Nd$_{1-x}$F$_3$ single crystals using magnetic susceptibility method.[8,9] A small change of the crystal field in La$_{0.9}$Nd$_{0.1}$F$_3$ with lowering temperature, as a result of temperature induced distortion of the crystal lattice (which caused a change in site symmetry of Gd^{3+} ions from C_{2v} at 77 K towards C_2 at 4.2 K) was observed in our most recent works.[7,10,1]

The purpose of the present paper is to study the crystal field in all samples at different temperatures using Electron Paramagnetic Resonance (EPR) technique and superposition model, because they are very sensitive to the distortion of the crystal lattice. Therefore surroundings of Gd^{3+} ions in the trigonal symmetry D_{3d}^4 with a hexamolecular unit cell were investigated. The spin-hamiltonian parameters (SHP) are analyzed in the light of the superposition model. Previously we studied local deformation in La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal.[7,11] Further, we extended the EPR measurements to temperatures covering the range 4.2 – 295 K in all chosen samples. The negative g shift of Gd^{3+}-doped La$_{0.9}$Ce$_{0.1}$F$_3$ and La$_{0.9}$Nd$_{0.1}$F$_3$ from that in the isostructural diamagnetic host LaF$_3$ indicates the antiferromagnetical ordering of Gd^{3+}-Ce^{3+} and Gd^{3+} - Nd^{3+} pairs.

2. CRYSTAL FIELD STUDY

The crystal field study has been performed by analyzing SHP's for Gd^{3+}-doped LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$, La$_{0.9}$Nd$_{0.1}$F$_3$ and PrF$_3$ single crystals in the temperature range 4.2 – 295 K, using the superposition model.[7,11] The above samples are the only crystals studied in detail for which well-resolved EPR spectra can be recorded down to liquid-helium temperature. Details of EPR measurements can be found elsewhere.[11] typical example of the spectrum and magnetic splitting of four Kramers

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doublets are presented in Fig. 1. The zero-field splitting (ZFS) of Gd^{3+} is defined as $\Delta E = E(\pm 7/2) - E(\pm 1/2)$ at magnetic field $B = 0$. The ZFS was determined on the basis of nine SHP's and plotted in Fig. 2. It can be seen that ZFS depends on the temperature as a parabolic function. The ZFS reaches maximum value at about 150 K for LaF_3, $La_{0.9}Ce_{0.1}F_3$ and $La_{0.9}Nd_{0.1}F_3$, whereas for PrF_3 the ZFS is increasing monotonically with lowering temperature down to 4.2 K. In Gd^{3+}-doped $LiYF_4$ crystal the ZFS also increased with decreasing temperature down to 4.2 K.[12] In order to explain such behavior of ZFS, the intrinsic parameter b_2 ($m = 0$) should be taken into consideration.[11] The ZFS and SHP varied linearly with the intrinsic parameter as determined from the superposition model. The intrinsic parameters b_2 for Gd^{3+}-doped samples in the temperature range 4.2 – 295 K are plotted in Fig. 3. The b_2 reaches minimum of negative values at about 150 K for LaF_3, $La_{0.9}Ce_{0.1}F_3$ and $La_{0.9}Nd_{0.1}F_3$, whereas for PrF_3 and $LiYF_4$ its negative values are continuously decreasing with decreasing temperature. The intrinsic parameter depends only on R_0 (the minimum distance between $Gd^{3+} - F^-$ ions corresponding to the 2-3 F^- pairs[7,11]). The R_0's depend on temperature similar to lattice constants[6] and reach minimum value at liquid-nitrogen temperature for Gd^{3+}-doped LaF_3, $La_{0.9}Ce_{0.1}F_3$ and $La_{0.9}Nd_{0.1}F_3$ (Fig. 4). On the other hand, for PrF_3 and $LiYF_4$ the R_0 is decreasing with decreasing temperature from 295 K to 4.2 K. Since the intrinsic parameter depends only on the R_0, it can be plotted versus R_0 (Fig. 5). The slightly change of R_0 with decreasing temperature causes drastic increase of b_2 in the temperature range below 150 K. Such behavior of the intrinsic parameter explains changes of SHP and ZFS. On the other hand, in PrF_3 and $LiYF_4$ there are not any drastic changes of the intrinsic parameter b_2 with R_0. Generally, the behavior is due to monotonic decrease of R_0 with temperature down to liquid-helium. We think that different behavior of the investigated samples is caused by critical temperature of the intrinsic parameter. The critical temperature of the intrinsic parameter does not depend on the structure of crystal lattice but individual character of lattice – the site symmetry of Gd^{3+} ion that is changed with temperature, as a result of temperature induced distortion of crystal lattice.
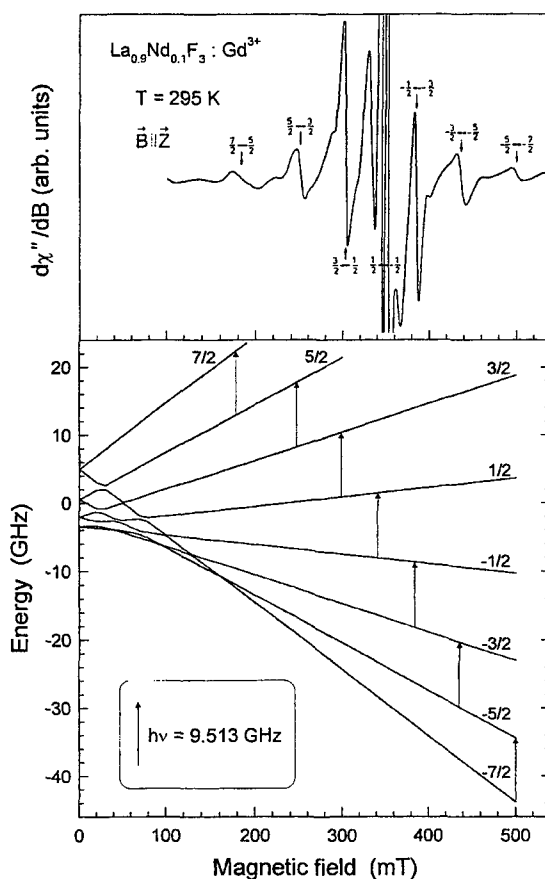

Fig. 1. EPR spectrum and energy levels of Gd^{3+}-doped $La_{0.9}Nd_{0.1}F_3$ single crystal at $T = 295$ K with $B \parallel Z$ (a-axis).
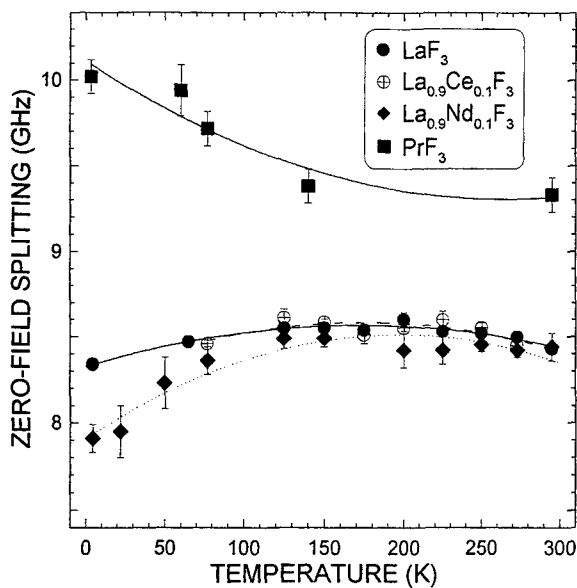
Fig.2. Temperature dependence of ZFS for Gd^{3+}-doped LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$, La$_{0.9}$Nd$_{0.1}$F$_3$ and PrF$_3$ single crystals.
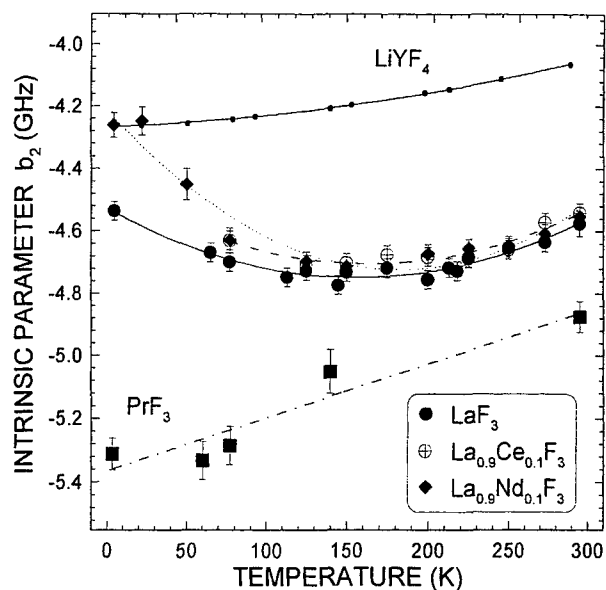

Fig. 3. Temperature dependence of the intrinsic parameter b_2 for Gd^{3+}-doped LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$, La$_{0.9}$Nd$_{0.1}$F$_3$, PrF$_3$ and LiYF$_4$ [12] single crystals.
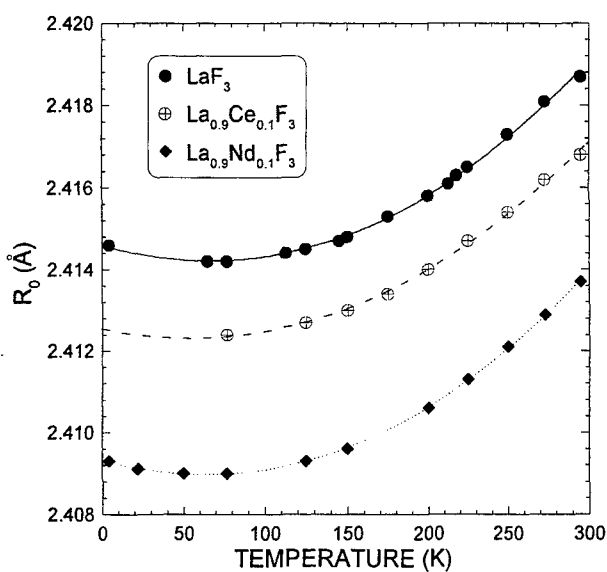

Fig. 4. Temperature dependence of the minimum distance R_0 between Gd^{3+} – F^- ions corresponding to the 2-3 F^- pairs[7,11] in LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$, La$_{0.9}$Nd$_{0.1}$F$_3$ single crystals.
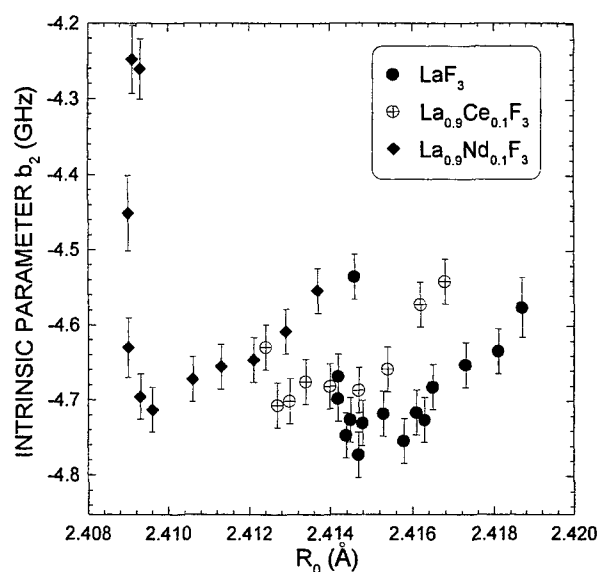

Fig. 5. The plot of the intrinsic parameter versus R_0 for Gd^{3+}-doped LaF$_3$, La$_{0.9}$Ce$_{0.1}$F$_3$ and La$_{0.9}$Nd$_{0.1}$F$_3$ single crystals.

3. CONCLUSIONS

New insight into the intrinsic parameter b_2 has been performed using superposition model. The critical temperature for intrinsic parameter has been proposed. The intrinsic parameter is very sensitive to the distortion of the site symmetry of Gd^{3+} ions. Although the variation of the distortion is small, it has a drastic effect on the intrinsic parameter b_2. The small distortion of the D_{3d}^4 trigonal symmetry has been observed in LaF_3, $La_{0.9}Ce_{0.1}F_3$ and $La_{0.9}Nd_{0.1}F_3$ below 150 K. Further, the distortion of the local site symmetry of Gd^{3+} ions from C_{2v} towards C_2 starts at 150 K and continuously increases with temperature decreasing down to 4.2 K, whereas in PrF_3 the distortion was not observed in the temperature range $4.2 - 295$ K.

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